

Advanced Anodes for Lithium-Ion Batteries

John Vaughey and Michael Thackeray, Electrochemical Technology Program
Chemical Engineering Division, Argonne National Laboratory

Introduction

As hybrid electric vehicles (HEVs) become more prevalent in the marketplace more emphasis is being placed on understanding the properties of the next-generation HEV battery system. In present HEVs, a nickel metal hydride (NiMH) battery is used, but significant advantages in power and capacity can be realized if a lithium-ion battery is used. In the car this would translate to better mileage (less car weight), better storage space (smaller battery packs), and increased performance (better power characteristics). We are investigating the limitations of the anode side of the battery. In present commercial Li-ion batteries, coated graphites are used; however, some abuse tolerance and capacity issues need to be addressed. We are investigating the properties of alternative systems--namely intermetallic alloys and metal oxides--and evaluating them using HEV testing parameters.

Challenges

Goal : Develop an alternative to the graphite-based anode system used for lithium-ion batteries in HEVs.

- Identify materials that can insert lithium reversibly at low potential and in sufficient amount to be useful in a practical battery.
- Display sufficient cycle life and low fade rate to compete against graphite-based systems.
- Have projected costs near present systems.

Intermetallic Electrodes

Emphasis: Intermetallic compounds (compounds constituted of metallic elements with a defined stoichiometry) have shown promise recently as negative electrodes for lithium-ion cells. The materials have been shown to work by two different mechanisms:

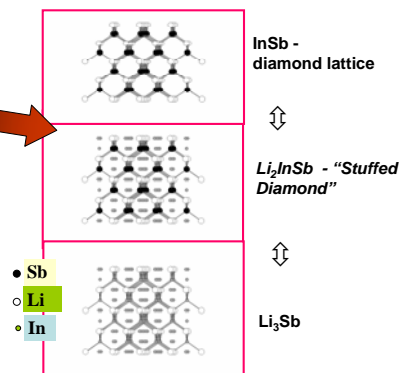
- 1) $x \text{ Li} + \text{MM}' \rightleftharpoons \text{Li}_x\text{MM}'$ - insertion
e.g. $10 \text{ Li} + \text{Cu}_2\text{Sn}_5 \rightleftharpoons 5 \text{ Li}_2\text{CuSn} + \text{Cu}$
- 2) $x \text{ Li} + \text{MM}' \rightleftharpoons \text{Li}_x\text{M} + \text{M}'$ - disproportionation
e.g. $8 \text{ Li} + \text{FeSn}_2 \rightleftharpoons \text{Fe} + \text{Li}_4\text{Sn}$

Studies of InSb Intermetallic Anodes

InSb is a III-V semiconductor based on a 4-bonded diamond net. Noting that Li_3Sb has a similar array of antimony atoms, we developed an in-depth understanding of the materials and electrochemical properties of Li_3Sb in relation to InSb using a combination of EXAFS/XANES, electrochemistry, X-ray powder diffraction, NMR, and other spectroscopies. We have identified several new classes of lithium-ion battery anodes and gained invaluable insight into this novel family of materials.

Results :

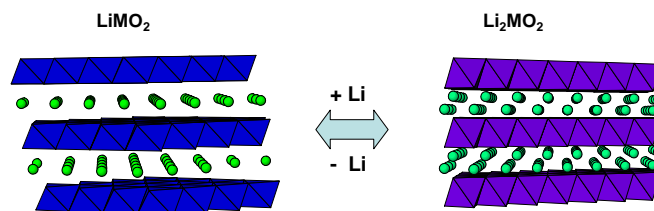
- We were able to demonstrate excellent capacities (>1500 mAh/cc) in excess of those of graphite-based anodes.
- InSb demonstrated excellent rate capability (good for power) and exceeded that of graphite under most conditions.



Low-Voltage Metal Oxides:

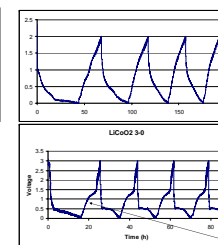
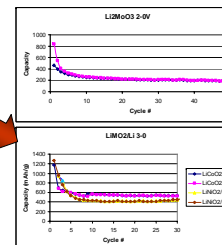
In general three classes of reactions with metal oxide anodes are known:

- Insertion reaction—lithium insertion into a stable oxide framework, e.g. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ or $\text{Li}(\text{Mn}_{0.5}\text{Ni}_{0.5})\text{O}_2$.
- Disproportionation reaction—lithium insertion leads to the formation of two metal oxides, e.g., $2 \text{ Li} + \text{Co}_3\text{O}_4 \rightleftharpoons \text{Li}_2\text{O} + 3 \text{ CoO}$
- Extrusion reaction—lithium insertion is accompanied by metal extrusion, e.g., $2 \text{ Li} + \text{CoO} \rightleftharpoons \text{Li}_2\text{O} + \text{Co}$.



Results: We investigated lithium insertion into layered metal oxides of stoichiometry LiMO_2 or Li_2MO_3 .

- Capacities were very high with the excess capacity (compared to theoretical) related to SEI layer formation.
- Materials displayed stable capacities in excess of 500 mAh/g.



Forms a Mo / Li_2O composite

In-situ XRD of plateau shows Co extrusion as Li_2O forms

$\text{CoO} + \text{Li}_2\text{O}$

Conclusions

- We have demonstrated that intermetallic anodes are a viable alternative to graphite in some applications for lithium-ion batteries.
- Metal Oxide anode systems based on displacement appear to have high irreversible capacities which may be overcome with other strategies. Insertion oxide materials have high stability but have higher than desired voltages.